



Photocatalysis assisted simultaneous carbon oxidation and NO_x reduction



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ABSTRACT

Photocatalysis assisted oxidation of carbon black was performed using TiO₂ photocatalyst under UV illumination in an atmosphere with NO, O₂ and water vapor at 150 °C. Carbon is oxidized mainly to CO₂ while NO is selectively converted to N₂. Enhanced O₂ and NO concentrations have a positive effect on the carbon oxidation rate. At a concentration of 3000 ppm NO and 13.3% O₂ in the gas phase the carbon oxidation rate reaches 2.3 μg_{carbon}/mg_{TiO2} h, at a formal electron/photon quantum efficiency of 0.019. HR SEM images reveal uniform gradual reduction of the carbon particle size irrespective of the distance to TiO₂ photocatalyst particles in the presence of NO, O₂ and H₂O.

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1. Introduction

Controlled oxidation of carbon nanoparticles is of interest to many practical applications. Regeneration of diesel particulate filters is a prominent example. A common filter regeneration strategy involves oxidation of the carbon deposit using NO₂ obtained by catalytic oxidation of NO emitted by the engine [1]. NO₂ mediated carbon oxidation proceeds at temperatures exceeding 250 °C, and NO₂ is reduced mainly to NO rather than N₂, necessitating an additional DeNO_x system downstream from the filter [1]. In nanotechnology, oxidative modification of carbon nanomaterials is needed for selective elimination of amorphous carbon debris, and for altering physico-chemical properties such as enhancing hydrophilicity. To this purpose carbon nanotubes (CNTs) are oxidized with concentrated mineral acid (e.g. nitric acid and sulfuric acid) to facilitate dispersion in polar solvents [2,3]. Graphitic oxide obtained by oxidation of graphite with the mixture of strong oxidants (nitric acid, sulfuric acid or potassium permanganate) [4,5]. Improved methods have been reported, concentrated acid and

strong oxidants are necessary for the oxidation process [6,7]. More sustainable chemical methods would be welcome [6].

Photocatalytic oxidation is mentioned among the green chemistry methods for sustainable development [8]. The method has been used to oxidize carbon, and for converting NO_x to N₂ various ways, and the possibility of combining both reactions has been suggested. Titanium dioxide is widely used for photocatalytic applications for its commercial availability and robustness [8]. UV light is needed for charge separation in TiO₂ semiconductor because of the large band gap of crystalline TiO₂ phases (anatase: 3.2 eV, rutile: 3.03 eV) [9]. Soot can be oxidized using sunlight-driven photocatalysis on TiO₂. Self-cleaning properties of TiO₂ coatings covered by soot have been demonstrated [10–16]. The efficiency of this photocatalytic process proceeding outdoors is, however, very low [10]. Oxidation of a 0.5 μm soot deposit requires e.g. 45 days [10,17].

NO_x elimination from air using photocatalysis is an emerging technology. Photocatalytic NO_x oxidation converts NO with O₂ to NO₂, which reacts further to nitrates that can be removed from the photocatalyst by water leaching. This deNO_x concept has been implemented e.g. on the surface of concrete pavement [18,19]. Titanium dioxide which is photoactive under UV light achieves photodecomposition of NO to N₂ and O₂ [8]. The reaction is slow and inhibited by O₂. Substantial N₂O by-product formation is observed [20–22]. Modified TiO₂ and zeolites have been investigated to

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improve catalyst activity and N_2 selectivity of the NO decomposition reaction with some success [23]. Additionally, the photo-SCR activity of commercial and modified TiO_2 in the presence of sacrificial reducing agents such as NH_3 , CO and short-chain hydrocarbon reductants has been demonstrated [24–32]. In nanotechnology, photocatalytic oxidation potentially is a sustainable method for the preparation of a variety of carbon materials such as oxidized carbon nanotubes and graphite oxide.

In a previous publication we reported that carbon black can be selectively photo-oxidized to CO_2 using NO in absence of O_2 [33]. Under those conditions in absence of O_2 , NO was converted to N_2 . The observed carbon oxidation rate was relatively low (ca. $2 \mu g_{\text{carbon}}/mg_{TiO_2} h$). In this paper we investigate the potential of photocatalytic oxidation of carbon using reactive gas mixtures with ppm quantities of NO in addition to O_2 . Promising results were obtained showing enhanced carbon oxidation rates and even oxidation of all carbon particles. Interestingly, NO is selectively reduced to N_2 even in the presence of O_2 . The size reduction of carbon particles up on oxidation is monitored with HR SEM.

2. Experimental

2.1. Sample preparation

Millennium PC500 (Cristal Global) was used as TiO_2 photocatalyst. This photocatalyst has a high surface area of $350 m^2/g$ and a primary particle (not aggregates) size of 9 nm [34]. The carbon black material was Printex U (Evonik) considered as a synthetic mimic of soot [35]. An amount of 5 mg of Printex U was deposited on glass plates ($430 mm \times 70 mm$) by spreading a suspension of Printex U in isopropanol. Samples were dried overnight at $120^\circ C$. 50 mg of TiO_2 catalyst powder was deposited on the soot coated glass plate from an isopropanol suspension afterwards.

2.2. Photocatalytic reaction

The photocatalytic reaction was carried out in a home-made flat photoreactor [33]. The prepared sample was illuminated from the top with a UV lamp (Rayonet) at a light intensity of $1.1 mW/cm^2$. Gases were fed from gas cylinders using mass flow controllers (Bronkhorst). More information concerning the experimental set-up and the gas analyzers can be found elsewhere [33]. The CO , CO_2 , NO_x (NO & NO_2) and N_2O content in the reactor volume are analyzed after the illumination period using UV spectroscopy and NDIR (ABB Limas 11HW and Uras 26 gas analyzers). The photoreactor was operated in batch type experiments as follows. The reactor was purged first under a flow of dry N_2 gas at $150^\circ C$ for 30 min. Subsequently, the reagent gas mixture was sent through the reactor in absence of light. After reaching the desired NO_x concentrations (measured using the NO_x analyser at the outlet), the gas inlet and outlet were closed. At the end of an illumination period, the product gas mixture was conducted to the gas analysers using carrier gas.

2.3. Quantification of nitrates

Quantitative determination of nitrates was performed on spent catalysts which were scraped from the glass plate. Nitrates were dissolved by slurrying the scraped powder in deionized water. Solids were removed by filtration. Dissolved nitrate was determined using a Hach Lange LCK 339 or 340 test kit. The conversion of NO to N_2 was determined from the N-atom balance over the reactor.

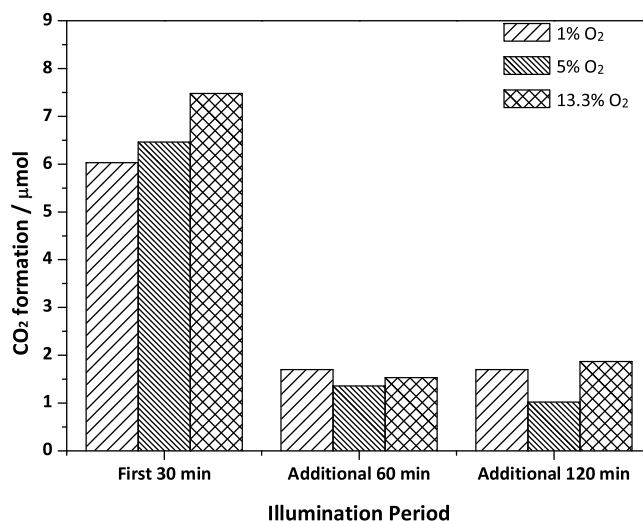


Fig. 1. CO_2 formation in photocatalytic oxidation of carbon black in presence of TiO_2 in a gas mixture with varied O_2 concentration and 3% H_2O .

2.4. Fourier transform infrared (FTIR) measurements

Fourier Transform Infrared (FTIR) spectra of scraped powder diluted in KBr (0.5 mg in 473 mg KBr) were recorded on a Bruker IFS 66 v/s.

2.5. High-resolution scanning electron microscopy (HR SEM) measurements

HR SEM images were recorded using low accelerating voltages (2 kV) with a Nova NanoSEM450 (FEI) equipped with BSE detectors, Concentric Backscattered detector (CBS), Through Lens Detector (TLD) combined with a beam deceleration mode (utilizing a stage bias up to 4 kV). The layer of carbon black and TiO_2 was deposited on an aluminium plate and imaged before and after carbon photo-oxidation. SEM images were taken on samples as such without any further modification.

3. Results and discussion

Printex U is commonly used as a model carbon material for investigating kinetics of carbon oxidation processes [36]. It is considered to be a good model for the elemental carbon portion of particulate matter emitted by diesel and gasoline direct injection engines [37,38]. A layer of 5 mg carbon black covered by 50 mg TiO_2 was exposed to UV light in a closed flat-plate photoreactor filled with gas mixtures containing 3% H_2O and O_2 at three different concentrations (1%, 5% and 13.3%). The reaction proceeded very slowly at room temperature and was accelerated upon heating. A reaction temperature of $150^\circ C$ was selected. The gas composition in the reactor was analyzed after illumination for 30 min. New gas was introduced and illumination continued for 60 min. The procedure was repeated for a third 120 min illumination period. The obtained photocatalytic oxidation of carbon to CO_2 is presented in Fig. 1. CO was always formed in much smaller quantities than CO_2 (typically only about 2% of the oxidized carbon, see Supporting information). Much more CO_2 was formed in the first illumination period compared to the second and third period. Increasing the O_2 concentration enhanced CO_2 formation especially in the first run. Printex U type carbon black contains a variety of carbon species including easily oxidized oxygenated groups [39]. This carbon fraction is oxidized first [37]. Refractory carbon representing the main share of carbon black is more difficult to oxidize [40–42]. Photocat-

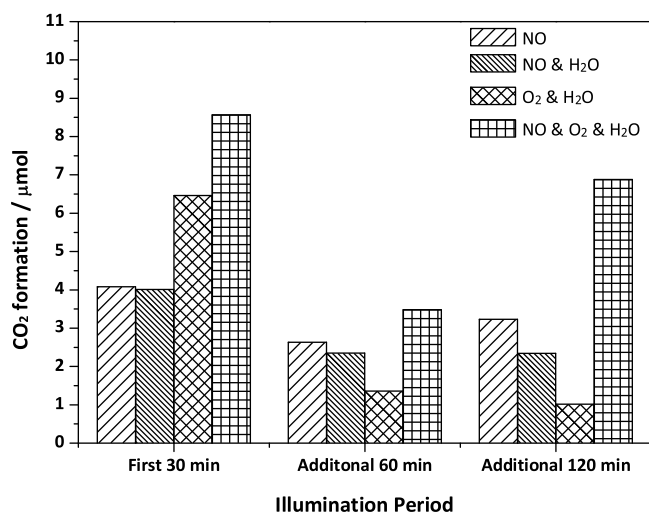


Fig. 2. CO₂ formation in photocatalytic oxidation of carbon black in presence of TiO₂ under different atmospheres. Concentrations: NO: 3000 ppm, O₂: 5%, H₂O: 3%. Fresh gas mixture introduced in the photoreactor before additional illuminations. The results in the presence of NO alone and of NO & H₂O were taken from previous publication for comparison [33].

alytic oxidation of the refractory carbon using O₂ and water only is slow. Under these reaction conditions, carbon oxidation probably proceeds via reaction with hydroxyl radicals (OH•) and superoxide anions (O₂^{•−}) formed from adsorbed water and molecular oxygen, respectively [11–15].

The composition of the gas atmosphere was altered in subsequent experiments and the influence of oxygen and water concentration studied (Fig. 2). With 3000 ppm NO in the gas phase without water and O₂, ca. 4.1 μmol CO₂ was formed in the first period. Replacing the gas and continuing illumination produced an additional 2.6 μmol of CO₂ a first time, and 3.2 μmol a second time. Adding 3% water to NO had no influence initially and decreased CO₂ formation in the second and third period (Fig. 2). In an atmosphere with 5% O₂ and water initially more CO₂ was formed (6.46 μmol). In the second and third illumination period little CO₂ was formed, viz. 1.36 μmol and 1.02 μmol (data from Fig. 1 added to Fig. 2), substantially less than with NO with and without water. Carbon oxidation went best in presence of both NO and O₂ (Fig. 2). In the first period 8.57 μmol CO₂ was formed, and 3.48 μmol and 6.88 μmol in the second and third period, respectively.

From this series of experiments it can be concluded that the first illumination period dealing with easily oxidized carbon of the carbon black material is most CO₂ productive, independent of gas composition which is in accordance with literature [37]. NO in the gas phase is essential to enhance CO₂ formation later in the reaction when refractory carbon is oxidized.

A key question is whether there is a synergetic effect of NO and O₂ in photocatalytic carbon oxidation. In the first period the formation of CO₂ in presence of both NO and O₂ amounted to 8.57 μmol, which is lower than the sum of CO₂ formed in presence of NO (4.1 μmol) and O₂ (6.5 μmol), suggesting competition rather than synergism. In the second run, there was no synergy either. Only in the third period combination of NO and O₂ generated an amount of CO₂ (6.88 μmol) exceeding the amount obtained with the two gases separately (3.22 μmol and 1.02 μmol, Fig. 2). This observation suggests that O₂ and NO compete initially for oxidation of the easily oxidized carbon, while they cooperate later on in the oxidation of the refractory carbon. Compared to the results in absence of oxygen, both oxygen and nitrogen monoxide have a positive effect on the amount of CO₂ formed.

Table 1

NO conversion and selectivity in carbon photooxidation.

Reaction	NO _x conversion (%)	Selectivity (%)			NO ₃ [−] (μg) ^a
		N ₂	N ₂ O	NO ₃ [−]	
First 30 min	99	78	11	11	1
Additional 60 min	99	80	1	19	2.6
Additional 120 min	97	99	1	0	2.4

Gas composition: 3000 ppm NO, 5% O₂, 3% H₂O.

^a Determined on scraped layer after reaction.

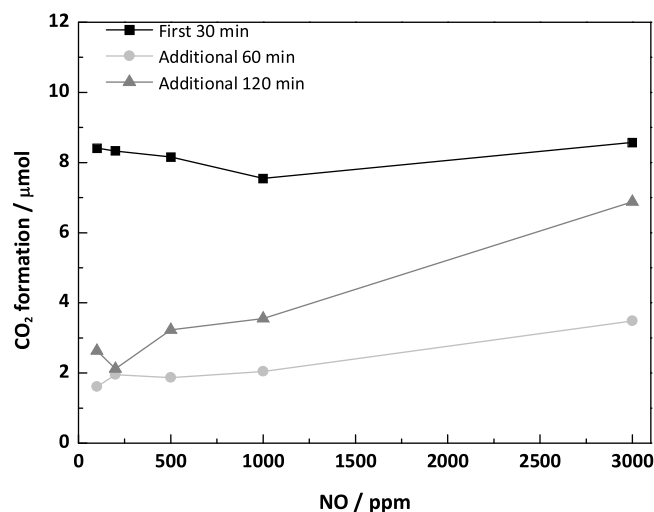


Fig. 3. CO₂ formation by photocatalytic oxidation of carbon black in the presence of TiO₂ in the presence of gas mixture with varied NO concentration and fixed concentrations of O₂ (5%) and water vapor (3%).

The obtained levels of NO conversion and the selectivity are reported in Table 1. After 30 min illumination of a fresh soot – TiO₂ layer in contact with gas mixture containing 3000 ppm NO, 5% O₂ and 3% water. NO_x in the headspace of the reactor was converted for 99%, with 78% N₂ selectivity, 11% N₂O and 11% nitrate (determined on scraped layer). The experiment was repeated on a new layer of soot and TiO₂. After 30 min illumination, the reactive gas was evacuated and new gas mixture introduced. After another 60 min illumination, the gas phase was analysed. 99% NO_x conversion was reached, with 80% N₂ selectivity, 1% N₂O and 19% nitrate. Finally, another fresh layer of soot and TiO₂ was loaded in the photoreactor, and subjected to the 30 and 60 min illumination procedure. A third illumination for 120 min resulted in 97% NO_x conversion, with 99% N₂ selectivity. The final nitrate content was 2.4 μg, similar to the content after 60 min. Apparently, no additional nitrate was deposited during the third illumination period.

The synergetic effect between NO and O₂ was further explored with an experiment in which the NO concentration in the gas mixture was varied while keeping the O₂ (and H₂O) concentration constant (Fig. 3). CO₂ formation in the first illumination period was rather insensitive to NO concentration, while in the second and especially in the third illumination periods, handling the more difficult to oxidize carbon, CO₂ formation increased with increasing NO content of the gas mixture. The tendency that more CO₂ is formed in the third illumination compared to the second initially observed at 3000 ppm (Fig. 3) is also observed at lower NO concentrations (Fig. 3). The longer duration of the third period (120 min) compared to the second one (60 min) may explain this difference. As mentioned previously, this carbon material contains easy to oxidize and hard to oxidize carbon. Therefore part of the carbon material were oxidized first at a relatively high carbon oxidation rate (in the first 30 min reaction in the presence of either oxygen or NO, Fig. 2).

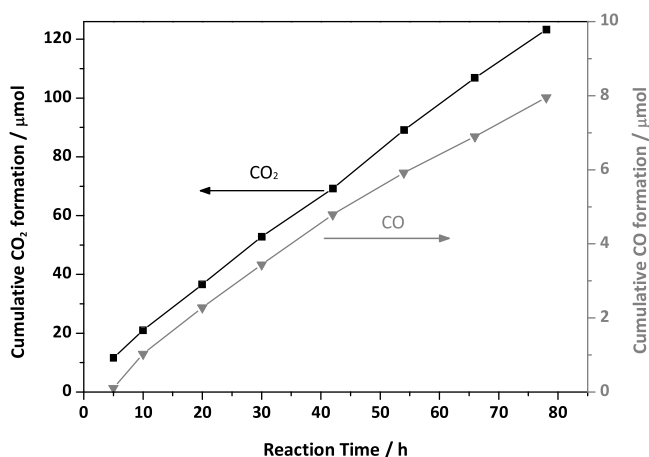


Fig. 4. Cumulative CO₂ and CO formation during a long carbon photo-oxidation experiment in the presence of NO, O₂ and H₂O. Gas composition; 3000 ppm NO, 3% H₂O, 5% O₂.

At this reaction stage, the carbon oxidation rate apparently cannot be increased by increasing the NO concentrations. In subsequent illumination periods, the remaining part of refractory carbon material is oxidized at a lower carbon oxidation rate. NO and O₂ have a synergetic effect on the oxidation of this type of carbon material, as shown in Fig. 2. Thus the carbon oxidation rate was effectively increased by increasing the NO concentrations in the third, 120 min illumination period.

In these experiments, in each illumination period NO was almost entirely converted. N₂O was formed especially in the first and second illumination periods in values similar to the values reported in Table 1. High selectivity to N₂ was obtained in the second and especially in the third illumination period.

The highest carbon oxidation rate of ca. 5.64 μg carbon per hour per mg TiO₂ was obtained in the experiment with 3000 ppm NO, 13.3% O₂ and 3% H₂O at 150 °C during the first 30 min for the easily oxidized carbon. For the refractory carbon an oxidation rate of 2.27 μg carbon per hour per mg TiO₂ was obtained in the third illumination period. Such reaction rate is rather low compared to thermal catalysis at higher temperatures (300–500 °C) (see Supporting information). The incident light intensity of the reactive layer in the photoreactor is about 2.9×10^{17} photons s⁻¹. An electron/photon formal quantum efficiency of 0.019 can be estimated from the formal quantum efficiency assuming carbon oxidation to be a 4-electron redox reaction. This value is higher than the reported photocatalytic oxidation of burning ‘T-lite’ soot on TiO₂ coating under UV irradiation in air (4.4×10^{-4}) [10].

A long experiment was performed with 78 h of continuous illumination (Fig. 4). Eight consecutive reactions were performed with UV exposure times ranging from 5 to 12 h, each time with a fresh gas mixture with 3000 ppm NO, 5% O₂ and 3% H₂O contacting the same soot-TiO₂ layer. In total 123.3 μmol CO₂ together with 7.9 μmol CO was formed (Fig. 4), corresponding to oxidation of about 30% of carbon loaded in the photoreactor. The carbon oxidation rate remained rather stable over this 78 h period.

The NO_x conversion was ca. 99% in each of the eight runs. Some N₂O was formed only in the first illumination (3%). In second and later illuminations N₂ was the only detected N-containing gaseous reaction product. The final nitrate content of the layer was 3.2 μmol and only slightly higher compared to the results obtained for shorter reaction times (Table 1).

The presence of nitrate on the samples after photocatalysis was confirmed with FTIR (Fig. 5). On a UV-illuminated layer of TiO₂ (without carbon) exposed to the reactive gas mixture a sharp absorption band at 1386 cm⁻¹ was observed (Fig. 5a). This sig-

nal was assigned to nitrate on the surface of TiO₂ photocatalyst [43]. The broad band around 3410 cm⁻¹ and the peak around 1635 cm⁻¹ were assigned to the stretching and bending vibrations of physisorbed water [15,44]. The broad peak centred at 530 cm⁻¹ was ascribed to bending of Ti–O bonds [45]. A layer of soot and TiO₂ exposed 78 h to UV light under reactive gas mixture showed a similar FTIR spectrum (Fig. 5b). In addition to these signals, a layer containing both soot and TiO₂ after reaction shows distinct IR absorption signatures that can be attributed to partially oxidized carbon. For instance in the spectrum of soot and TiO₂ subjected to three runs (Fig. 5d), absorption at 1260 cm⁻¹ can be attributed to the C–O–C stretching in an anhydride or aryl ether linkage [46]. The signal around 1100 cm⁻¹ can be assigned to C–C and C–H plane deformation of aromatic groups [47]. The band at 800 cm⁻¹ could be ascribed to the C–H out-of-plane bending of highly substituted aromatic compounds [46]. The small peak at 2918 cm⁻¹ is due to the C–H asymmetric stretching vibrations [46].

Under UV illumination, nitrate is formed on the TiO₂ surface from the reaction of nitric oxide with photo-generated hydroxyl radicals [48]. NO₂ is formed as an intermediate which could be further oxidized into nitrate by •OH radicals. However, the formed nitrates can be consumed by the reaction of HNO₃/NO₃⁻ with NO in the presence of TiO₂. Therefore, formation and decomposition of nitrate on TiO₂ is a dynamic process and steady-state concentration in the layer reflects the dynamic equilibrium of nitric acid formation and transfer to the carbon surface via the gas phase. The N₂O formation on fresh TiO₂ has been explained by reaction of NO on photo-generated Ti³⁺ centers. When the TiO₂ surface is covered by nitrate less of these sites are available, which could explain why N₂O formation is suppressant in second and third illumination periods.

Size reduction of the carbon black particles during photocatalysis assisted oxidation was investigated with HR SEM (Figs. 6 and 7). To this purpose TiO₂ and carbon were deposited on aluminum support for SEM and treated in the photoreactor. The large white aggregates on the SEM pictures are TiO₂ particles. The small grey spheres are carbon particles. The initial size of original carbon black particles (not aggregates) measure 45 ± 7 nm. With progression of the photocatalysis assisted oxidation, changes of the carbon particle size were observed. After 10 h reaction in the presence of 5% O₂ and 3% H₂O, some of the carbon particles near TiO₂ photocatalyst were reduced in size (Fig. 6). After 24 h reaction, most of the carbon particles in the vicinity of TiO₂ were even more reduced in size and in some areas, carbon particles were no longer present (Fig. 6). Carbon particles at longer distance from TiO₂ aggregates retained their original size. In photocatalytic oxidation reactions on TiO₂ it is well known the substrate does not need to be adsorbed on the TiO₂ surface. Remote or lateral photocatalytic oxidation of organic substrate has been reported. For instance, remote bleaching of dyes and oxidation of organic compounds was observed in a photoreactor in which TiO₂ and dye were coated on opposing surfaces separated by a small gap (12–50 μm) [49,50]. Oxygen-containing functional groups were introduced in polystyrene by the remote oxidation in such photoreactor [50]. In another experiment, soot deposited alongside TiO₂ film was oxidized preferentially and the gap distance between the soot and TiO₂ increases with the irradiation time [14]. This lateral oxidation process was attributed to the migration of the photo-generated oxidizing species toward the carbon particles.

Remote soot oxidation was also observed with ‘T-lite’ candle soot layer spaced by 175 μm from a TiO₂ coating [11]. Oxidation of soot was observed in the area where the soot was opposing the TiO₂ coating and progressed very slowly further away from TiO₂. A similar observation was made in this work. Carbon particles at distances of ca. 3 μm from TiO₂ remained intact.

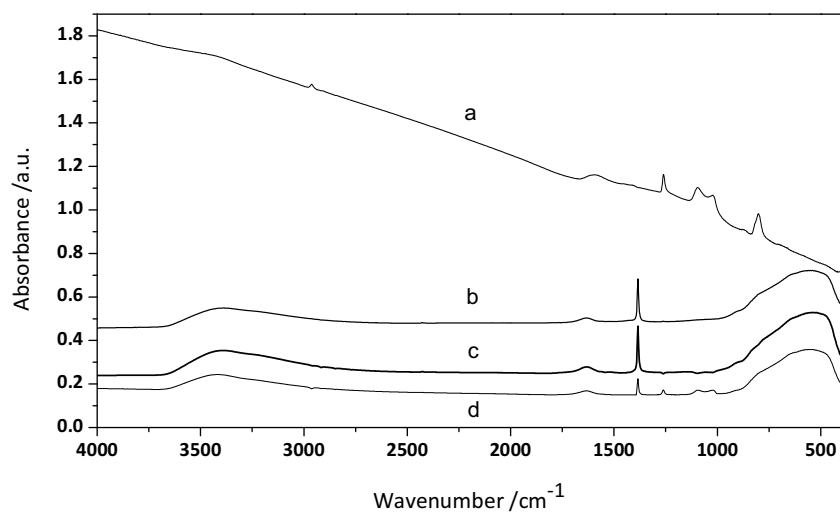


Fig. 5. FTIR spectra of scraped powder from the support glass: (a) carbon black before reaction; (b) nitrate-saturated TiO_2 photocatalyst layer (without carbon) after 3 h exposure to a gas mixture with 3000 ppm NO , 5% O_2 and 3% H_2O (30 ml/min) under UV light at 150°C ; (c) carbon black– TiO_2 layer after 8 consecutive reactions (total reaction time of 78 h); (d) carbon black– TiO_2 layer after three consecutive NO_x reductions (experiment of Table 1).

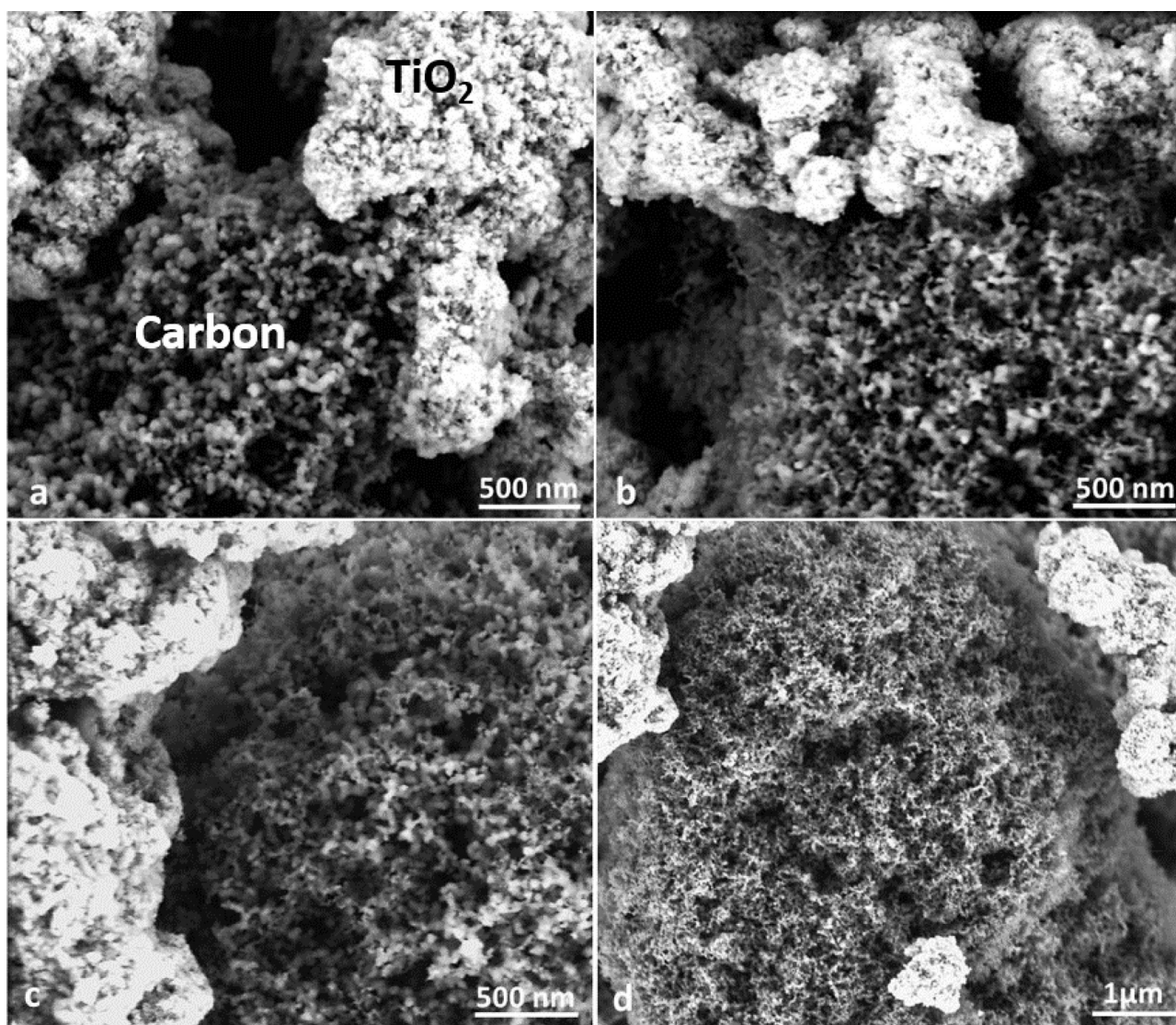


Fig. 6. HR SEM images of samples deposited on aluminium plate. (a): before reaction; (b): after 10 h UV irradiation; (c) and (d): after 24 h UV irradiation under an atmosphere with 5% O_2 and 3% H_2O at 150°C . White aggregates = TiO_2 ; small grey spheres = carbon particles.

A different picture emerged when photocatalytic carbon oxidation was performed in presence of NO and O₂ (Fig. 7). The size of the carbon particles was uniformly reduced. After 10 h continuous exposure to UV light in the presence of reactive gas mixture, the carbon particle size was reduced to 28 ± 7 nm. After 24 h of reaction the carbon particle diameter was further reduced to 17 ± 4 nm. General inspection of the sample with HR SEM revealed homogeneous carbon particle size reduction, a gradual fining of the carbon particle network was observed independent of the distance to TiO₂ particles. Apparently, contact between carbon and TiO₂ is not needed for achieving carbon oxidation and gaseous reaction intermediates must be involved spreading better than in absence of NO_x. Oxidizing species generated in the presence of nitric oxide, oxygen and water are postulated to be migrating over longer distances to reach the carbon surface than in the absence of nitric oxide. This hypothesis is based on the CO₂ formation data (Fig. 2) and the HR SEM observations (Figs. 6 and 7) which were obtained in the experiments in the presence or absence of NO. In the presence of NO (Fig. 2), more CO₂ was formed especially in the second and third illumination periods than in the experiments in absence of NO. This means the gas mixture with NO can oxidize more carbon particles than the experiments only with oxygen and water. From the HR-SEM pictures (Fig. 6, after reaction in the presence of O₂ and H₂O) it could be evident that, in absence of NO, carbon particles close to TiO₂ were more oxidized than distant carbon particles, and the carbon particles at distances of ca. 3 μ m from TiO₂ remained intact after reaction. From the HR SEM pictures (Fig. 7, in the presence of NO, O₂ and H₂O) it is seen that, in the presence of NO, carbon particles close to or far from TiO₂ were uniformly reduced in size after reaction. In the presence of oxygen and water, the photo-generated hydroxyl radicals and oxygen related radicals are assumed to be the oxidizing species for carbon photo-oxidation. In the presence of NO, O₂ and H₂O, besides the hydroxyl radicals and the oxygen related radicals, nitrogen containing species could also be oxidizing agents. From these observations we postulate that the oxidizing species formed in the presence of NO can migrate longer distance than hydroxyl radicals and oxygen related radicals which are formed in the presence of water and oxygen (without NO). These air-borne or surface-mobile species may be nitrogen containing species such as nitric acid or nitrous acid. Further investigation is needed to identify this species.

A potential use of simultaneous carbon oxidation into CO₂ and NO_x reduction to N₂ obviously is exhaust gas purification. Currently, particulate matter is removed via a particulate filter, while NO_x is reduced to N₂ via a NO_x storage and reduction catalyst or via selective catalytic reduction (SCR). Photo-SCR of NO_x using NH₃ (Photo-NH₃-SCR) reductant has been demonstrated [51]. Here we present Photo-C-SCR, i.e. the photocatalysis assisted reduction of NO_x to N₂ using carbon as reductant. Simultaneous removal of NO_x and PM at low temperature is very attractive. The obtained carbon oxidation rates are only a small fraction of current state-of-the-art thermal carbon oxidation catalysts at 300–500 °C (carbon oxidation rates using thermal catalysis from literature are provided in Supporting information).

This work suggests that oxidative modification of carbon nanomaterial may also be achieved using photocatalysis. Carbon black is a synthetic nanopowder of elementary carbon produced in large tonnage for use as a pigment and as a filler material to improve heat and electric conductivity, UV light absorption and mechanical properties [36,52,53]. Controlled size reduction using photocatalysis has been achieved (Fig. 7). Carbon nanotubes (CNTs) are often chemically modified via the oxidation with nitric acid to increase their dispersability in water, methanol, or other polar solvents [54]. Treatment of CNTs with boiling nitric acid for 16–48 h is a common procedure [55,56]. Over 60% of the CNTs can be lost after the treatment [2]. Similarly, graphite oxide is generally obtained by

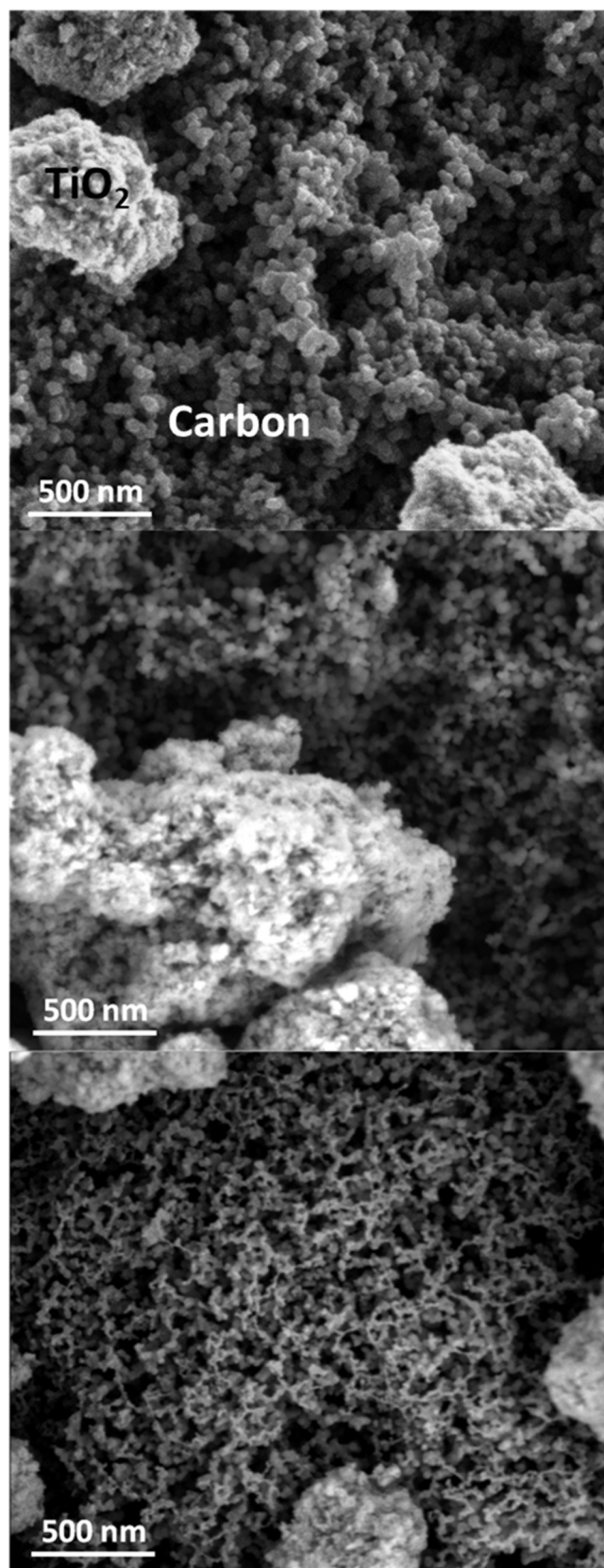


Fig. 7. HR SEM images of samples deposited on aluminium plate (taken at same magnification). Upper: before reaction, Middle: after 10 h UV irradiation, Under: after 24 h UV irradiation under an atmosphere with 3000 ppm NO, 5% O₂ and 3% H₂O at 150 °C. White aggregates = TiO₂; small grey spheres = carbon particles.

treating graphite with strong oxidants such as in Hummers' method using a mixture of sulfuric oxide, sodium nitrate, and potassium permanganate to oxidize graphite [5]. Formation of gaseous (NO_x) and aqueous waste streams render the method hazardous and unsustainable [6]. Here we have shown oxidation of carbon nano-materials can be achieved by photocatalysis under mild reaction conditions limiting the use of hazardous chemicals and byproduct formation. The potential of this method needs further investigation.

4. Conclusions

Commercial TiO_2 (Cristal Global PC500) is active in photocatalysis-assisted oxidation of carbon black with nitric oxide and oxygen in the presence of water vapor at 150°C . Carbon is selectively converted into CO_2 while NO_x is reduced to N_2 . Up to 30% of the carbon was oxidized without catalyst deactivation. Uniform size reduction of the carbon particles in the presence of NO , O_2 and H_2O was observed with HR SEM, irrespective of the distance to TiO_2 photocatalytic particles suggesting the involvement of mobile oxidative species.

Photocatalysis assisted carbon oxidation and NO_x reduction may find application in exhaust gas purification. The reduction of NO_x selectively to N_2 using carbon is a new type of SCR catalysis, coined Photo-C-SCR. The highest observed carbon oxidation rate of $5.64\ \mu\text{g}$ carbon per hour per mg TiO_2 is much below carbon oxidation rates obtained with thermal catalysts in the temperature range $300\text{--}500^\circ\text{C}$. At low temperature where thermal catalysts are inactive, photocatalysis may be relevant provided activity is further enhanced.

Photocatalysis assisted oxidation may be an alternative method for modification of carbon nanoparticles. But more work is needed to explore this idea.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.09.042>.

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